



Supercritical ethanolysis for biodiesel production from edible oil waste using ionic liquid [HMim][HSO₄] as catalyst



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ABSTRACT

Catalytic ethanolysis of waste cooking soybean oil using the ionic liquid [HMim][HSO₄], as catalyst, to yield ethyl esters has been investigated. The ionic liquid, labeled as IL, showed stability under high conditions of temperature and pressure. Transesterification temperature was monitored and was maintained constant. The contents of ethyl esters in all samples were determined through GC (by normalization method) and ¹H NMR techniques. Highest yield (97.6 %) was obtained after 45 min of reaction, at 528 K under 9.62 MPa in the presence of 0.35 mL of IL. The transesterification did not occur with high yielding using the same conditions but in absence of the catalyst. The presence of water in reaction medium, in the range of 1.0–3.0% (v/v) due to ethanol impurity, does not affect the ethyl esters yield. The method proposed in this paper is advantageous over others reported in the literature due to the lower reaction time required and the higher biodiesel yield. The results showed that the biodiesel production by transesterification through supercritical ethanolysis is environmental-friendly and presented promising perspectives.

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1. Introduction

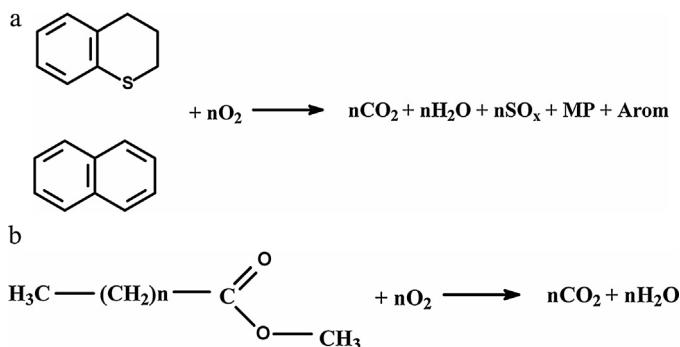
Diesel is a fuel of complex composition and largely used in transport vehicles, farming, industrial and commercial sectors, to generate potency and mechanic energy. This oil has, as main components, paraffinic, olefinic and aromatic hydrocarbons and by-components (impurities) substances having sulfur, nitrogen and metallic atoms [1,2]. Biodiesel is an alternative fuel to diesel engines. Furthermore, it is renewable, biodegradable and non-toxic. Fatty acids alkyl esters of long chains are produced through transesterification reaction between alcohol and animal fat or vegetal oils [3,4]. Biodiesel is considered more environmental friendly than diesel because it presents reduced emissions of sulfur compounds (SO_x) and particulates based on phosphorus (P) compounds. The combustion reactions for diesel and biodiesel are shown in Scheme 1 [5].

Reaction-catalyzed systems developments are being constantly reported and there is a requirement about the products (that should be easily purified) and the catalysts (that should be recovered) [6]. Replacement of acidic liquid catalysts for nontoxic, non-corrosive, easy-to-handle and environmental friendly compounds is a pursuit in the field of catalysis. In this direction, ionic liquids, IL, are profitable from both economic and practical points of view [7].

The Belgian patent of 1937 (n. 422,877), entitled 'Procédé de transformation d'huiles végétales en vue de leur utilisation comme carburants' [granted to Brussels University's researcher Charles George Chavanne] showed the first reporting of what nowadays we call biodiesel [8]. In such study, ethylic esters were obtained from palm oil by transesterification in acidic medium. However, the term biodiesel was published for the first time lastly, in 1988, in a Chinese work entitled 'Development of biodiesel fuel' [9–11]. Nowadays, vegetal oil biodiesel can be produced by several methods such as microemulsions, pyrolysis, catalytic cracking and transesterification, being the last the most promising and used method [12,13].

Transesterification reaction can be performed under homogeneous medium using acid or basic catalysts. In the basic catalysis,

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Scheme 1. Combustion reactions of (a) Diesel and (b) Biodiesel. MP means microparticulates. Arom means not or partially reacted aromatic compounds. Based on J.V. Visentainer and O.d.O.S. Júnior's book [5].

the saponification reaction results in products with difficulties in purification. This problem is not remarkable in the acidic reaction, but the reaction occurs in lower speed [14]. Transesterification at room temperature and ambient pressure is relatively low due to two-phase formation between oil and alcohol. However, biodiesel production can be accelerated using, or not, catalyst when the alcohol is under supercritical conditions [15,16].

Products obtained from the oil transesterification reaction under supercritical ethanol (scEtOH) are primarily monoalkyl esters of long chain fatty acids (biodiesel), glycerol as by-product and, depending on the used stoichiometry, either monoglycerides, diglycerides as reaction intermediates [17]. The general transesterification reaction of oil (triglyceride) by an alcohol is shown in **Scheme 2**.

The quantification of formed esters can be made through many techniques, such as ^1H NMR spectroscopy [18–20], gaseous chromatography (GC) [21–23], among others. In addition, this can be done using different ways, through a calibration curve, standard addition and normalization, as examples. For instance, studying impurity components of amphetamine, Pikkraiinen showed that normalized results of GC were accurate; data processing studies for further pattern recognition studies indicated superiority of data normalization over quantitation [24]; also Bicchi et al. reported accuracy data by characterizing components of peppermint oil, where ultrafast module-GC and conventional GC normalized areas percentage were perfectly comparable [25].

Supercritical fluids are largely used in research. Related studies started in 1879 and a model describing the solubility in this condition was proposed in 1907 [26,27]. Solvents possess advantages in supercritical conditions, due to changes in solvent density and solvation power [28,29]. Conversion of oils to methyl esters using supercritical conditions started in the beginning of 2000's in Japan using basic catalyst [30].

Brazil is one of the most important ethanol producer. Ethanol is renewable and non toxic, thus can be used as alternative to methanol in the fatty acids transesterification process.

To overcome some difficulties related to transesterification reaction speed at ordinary temperature and pressure conditions, new methodologies using alcohols in supercritical conditions has been proposed [31,32]. Procedures using IL as catalysts and/or solvents have been developed [33]. ILs are considered "green solvents" that attract great interest due to its distinctive characteristics: such as possibility for compound optimizing through a good selection of cations and anions, thermal and electrochemical stability, non volatility, low inflammability [34,35]. In this way, ILs have been largely used in the extraction, catalysis [36,37], electrochemistry [38] and organic synthesis [39,40]. ILs have melting points frequently smaller than 373 K, possess low viscosity and vapor pressure and usually are derivative from 1,3-dialkylimidazolium

with counter ions that can be PF_6^- , BF_4^- , CF_3SO_3^- etc. Furthermore, to be used as catalysts, IL should be soluble in the ionic phase and not in organic solvents. Then an organic solvent can be used to extract the formed organic products [41] allowing separation of catalyst.

In this study the IL 1-hydrogen-3-methylimidazolium hydrogen sulfate ([HMim][HSO₄]) was used as catalyst for the transesterification reaction of soybean waste oil under supercritical ethanol (scEtOH). The aim of this work was to determine the influences of reaction time and amount of water on yield of the biodiesel produced through the reaction catalyzed by [HMim][HSO₄]. The recovering of used catalyst was also evaluated.

2. Experimental

2.1. Synthesis of [HMim][HSO₄]

The [HMim][HSO₄] was synthetized according to the method described by Hajipour et al. [42]. For this, a 1-methylimidazol solution (1.59 mL, 20 mmol) was prepared in acetonitrile (5 mL) and maintained at close to 273 K, under stirring. Over this solution concentrated sulfuric acid (1.03 mL, 20 mmol) was added, drop-to-drop. The reaction was maintained under stirring for further 3 h (1 h at 273 K and 2 h at room temperature). In the end of the reaction time, the obtained IL was washed repeatedly with ethylic ether (3 × 5 mL), to remove any non ionic residues and, then, dried under reduced pressure (0.4 kPa) at room temperature for 24 h. The 1-hydrogen-3-methylimidazolium hydrogen sulfate was obtained like colorless and viscous oil, with high purity (as will show after).

2.2. Ionic liquid stability in scEtOH

The IL [HMim][HSO₄] was exposed to ethanol at room temperature (ca. 298 K) and ambient pressure conditions (ambEtOH) and also to ethanol under supercritical conditions (scEtOH), both during 45 min. To evaporate the excess of ethanol and remove ethanol/water residues, vacuum oven (Marconi, MA 030/12, Piracicaba, SP, Brazil), set at 313 K and reduced pressure of 20 kPa; and lyophilizer (Martin Christ, Alpha 1-2 LDs Plus, Germany) set at 233 K and reduced pressure of 0.4 kPa were used, respectively.

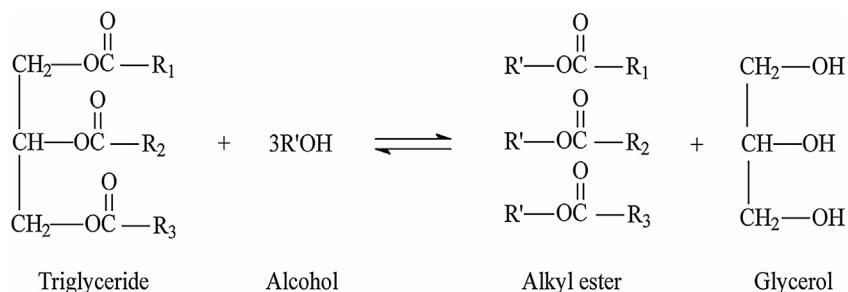
FTIR spectra (Perkin Elmer model Frontier, São Paulo, Brazil) in the range of 4000–400 cm^{-1} ; ^1H NMR spectra (Varian model Mercury Plus, Palo Alto, CA, USA) operating at 300 MHz (DMSO-d₆, Cambridge Isotope Laboratories Inc, Andover, MA, USA); and Mass spectra (Micromass, model Quattro micro API, Beverly, Massachusetts, USA) were acquired and analyzed in order to confirm the stability of IL.

2.3. Acquisition and samples preparation of soybean waste oil

Soybean oil was purchased in a local supermarket (Maringá, PR, Brazil); waste sample of this soybean oil was generated by submit a given amount of oil to six cycles (10 min, 453 K). Soybean oil and soybean waste oil samples were used in the transesterification reactions. Before the reaction, the sample was previously heated up to 373 K for 20 min to remove the moisture. Therefore, it was filtered with paper filter in simple funnel to remove any solid impurity.

2.4. Transesterification of soybean waste oil under scEtOH catalyzed by [HMim][HSO₄]

Transesterification process was performed according to the methodology described by Nunes et al. [43] for PET depolymerization and using the same apparatus. Reaction was carried out in a 0.1 L home-made batch-type reactor made of 316[®] stainless steel,



Scheme 2. Transesterification reaction of a triglyceride and alcohol (R'OH).

Table 1
Conditions used on different runs for transesterification reaction.

Run	Time reaction (min)
1	45
2	30
3	15
4	0
5 ^a	45

Experimental condition: pressure: 9.62 MPa; temperature: 528 K; volume of catalyst: 0.35 mL; volume of ethanol: 60 mL; mass of waste oil: 1.5 g.

^a Recovered catalyst.

equipped with inlet and outlet valves, a manometer, a thermometer, and a heating collar controlled by a programmable temperature (528 K, with a precision estimated to ± 5 K, measured by a J-type thermocouple) [28].

For the experiments, 1.5 g of oil, 60 mL of anhydrous ethanol and 0.35 mL of [HMim][HSO₄] were added to the reactor vessel at room temperature and heated (rate of about 8 K min⁻¹) to a reaction temperature of 528 K. Reactor pressure (9.62 MPa) was attained by nearly filling the vessel with desired amount of oil, ethanol and ionic liquid and keeping the reactor properly closed, avoiding the need of using pressurized gas for the ethanol to reach supercritical conditions. After requested reaction time (see Table 1 for time reaction used in each run), the heating collar was removed and the vessel submitted to a quenching to be quickly cooled to room temperature using water and ice.

For evaporating the ethanol excess, in each run, the sample was transferred from the reaction vessel to a beaker that was placed inside a vacuum oven (Marconi, MA 030/12, Piracicaba, SP, Brazil) set at 313 K and reduced pressure of 20 kPa. IL and glycerol were separated from the main product (biodiesel) by washing the samples with distilled water. The resultant biodiesel was filtered using Na₂SO₄, paper and a simple funnel, to remove water excess.

2.5. Method for recovering the ionic liquid

The IL [HMim][HSO₄] remaining in the water used for biodiesel washing was recovered by water evaporation in a vacuum oven set at 313 K and reduced pressure of 20 kPa, and then lyophilized at 228 K and 0.4 kPa for 48 h. Part of IL was reused in a further run and part used for FTIR, ¹H NMR and Mass Spectrometry (MS) analyses.

2.6. Quantification of biodiesel by GC analysis

Total esters were determined using a Thermo TRACE CG Ultra gas chromatograph, equipped with PTV (Programmed Temperature Vaporizing) injector and auto sampler. The protocol is based on a previous work by Santos Júnior et al. [44]. A 5% phenyl fused silica capillary column (10.0 m \times 0.32 mm ID \times 0.1 μ m film thickness) was connected to an uncoated, deactivated 5.0 m \times 0.53 mm ID fused silica pre-column with a press tight fitting. The column

was maintained at 323 K for 1 min, followed by a heating rate of 10 K min⁻¹ until 453 K. Then, it was once again raised to 503 K at a rate of 7 K min⁻¹. Finally, after this period the column was heated to 643 K at a rate of 10 K min⁻¹ and maintained for 8 min. The injector was maintained at 333 K for 1 min, followed by a heating rate of 14.5 K min⁻¹ until 643 K, which was maintained for 30 min. Detector was kept at 643 K. The flow rates (in mL min⁻¹) for the carrier (H₂), auxiliary (N₂) and detector flame (H₂ and synthetic air) gases were 1.2, 30.0, 35.0 and 350, respectively.

Aliquot of 1.0 μ L was injected in the chromatograph for posterior quantification. The peak areas relative to fatty acid ethyl esters was determined using the software Chrom Quest 5.0 (Enterprise). Quantification was done according to the method proposed by Visentainer and Franco [45], where the relative percentage of a specific ethyl ester was calculated through correlation between the sum of all the compounds areas obtained on the chromatogram.

2.7. Quantification of biodiesel by ¹H NMR analysis

¹H NMR spectra were obtained using a Bruker spectrometer, model Avance III HD (500 MHz). Samples were dissolved in 0.6 mL of deuterated chloroform (CDCl₃; Cambridge Isotope Laboratories Inc., Andover, MA, USA) and transferred to an NMR probe (5.0 mm internal diameter). Spectra were recorded at room temperature and the NMR parameters were: 20 ppm (10 kHz) spectral width; 1 s relaxation delay; 30° pulse width; 64 scans, and 3.28 s acquisition time.

3. Results and discussion

3.1. Stability of [HMim][HSO₄]

Just after prepared, the [HMim][HSO₄] is a colorless and transparent liquid, but after be submitted to scEtOH for 45 min it became greenish. In order to evaluate if its chemical structure is affected or not by the exposure to scEtOH, despite the change in color, considering that thermal stability under scEtOH is a mandatory request for using as catalyst under this condition [46], the IL [HMim][HSO₄] sampled after exposure to scEtOH for 45 min was analyzed through FTIR, ¹H NMR and MS and compared to respective spectra obtained using IL [HMim][HSO₄] not exposed to scEtOH.

FTIR and ¹H NMR spectra of the [HMim][HSO₄], before and after exposure to scEtOH (at 9.62 MPa and 528 K) for 45 min were obtained and are presented in Figs. 1 and 2, respectively.

Comparing the [HMim][HSO₄] FTIR spectrum before and after scEtOH exposure, no changes were observed in the [HMim][HSO₄] due to scEtOH exposed. The FTIR spectra of [HMim][HSO₄] show bands between 3500 and 3100 cm⁻¹, attributed to N–H stretch, merged to bands related to hydrogen bonds from –OH of ethanol molecule. At 3147 cm⁻¹ there is a band attributed to aromatic C–H bond and bands at 2965.2 and 2866.5 cm⁻¹ due to aliphatic asymmetric and symmetric C–H stretching vibrations. At 1641.5 cm⁻¹

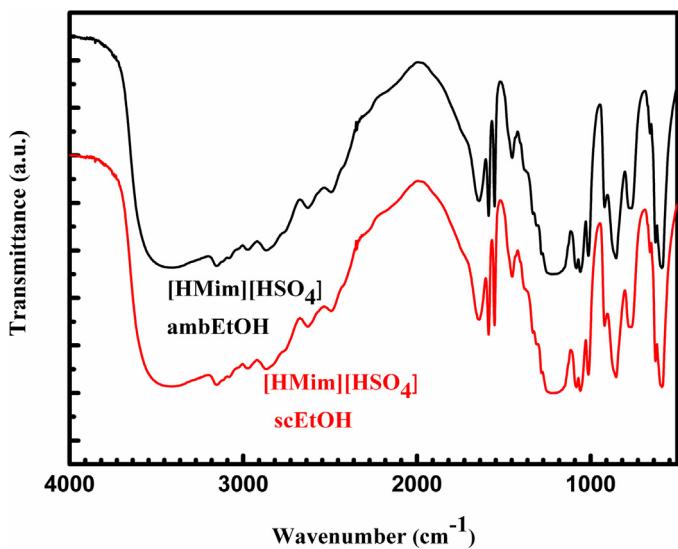


Fig. 1. ^1H NMR spectra of $[\text{HMim}][\text{HSO}_4]$ in ambEtOH and after 45 min of exposure at scEtOH. (300 MHz, DMSO, ppm).

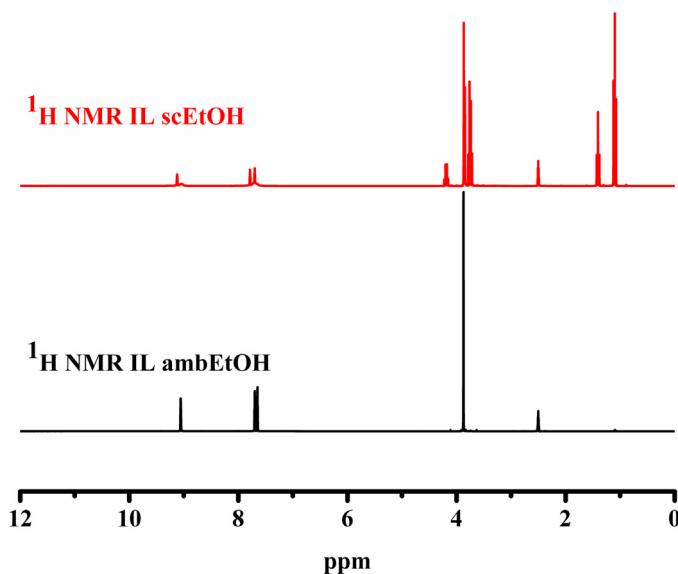


Fig. 2. ^1H NMR spectra of $[\text{HMim}][\text{HSO}_4]$ in ambEtOH and after 45 min of exposure at scEtOH. (300 MHz, DMSO, ppm).

there are bands associated to stretch of $-\text{CH}_2-$ groups. Bands of strong intensity between 1600 and 1550 cm^{-1} are associated to N–H bending. The band at 1451.4 cm^{-1} is due to ethylene groups ($\text{C}=\text{C}$) bending. Bands at 1260.5–1161.1 cm^{-1} range are related to C–N aromatic stretch; the band at 1053.6 is due HSO_4^- stretching [47–49] of IL.

The ^1H NMR spectrum (300 MHz, DMSO- d_6 , ppm) of $[\text{HMim}][\text{HSO}_4]$ not exposed to scEtOH (Fig. 2) presents the following signals: 3.86 ppm (s, 3H), 7.64 ppm (t, 1H), 7.69 ppm (t, 1H) and 9.06 ppm (s, 1H). The signal at 3.86 ppm was attributed to hydrogen atoms in the methyl group coupled at the imidazolium ring; the signals at 7.64 and 7.69 ppm were attributed to hydrogen atoms of the imidazolium ring; the signal at 9.05 ppm was attributed to the hydrogen of imidazolium ring that is located between two nitrogen atoms in the IL structure.

Compared to ^1H NMR spectrum of $[\text{HMim}][\text{HSO}_4]$ not exposed to scEtOH, the ^1H NMR spectrum of $[\text{HMim}][\text{HSO}_4]$ exposed to scEtOH (Fig. 2, 300 MHz, DMSO- d_6 , ppm) showed four additional signals at

δ : 1.10, 1.40, 3.75 and 4.18 ppm beyond the signals already observed in the ^1H NMR spectrum of not exposed $[\text{HMim}][\text{HSO}_4]$ despite some of them suffered small shifts: 7.64–7.70 ppm; 7.69–7.79 ppm; and 9.0–9.12 ppm. So, the signals observed in the ^1H NMR spectrum of not exposed IL $[\text{HMim}][\text{HSO}_4]$ remained present in the spectrum of IL exposed to scEtOH.

Additional signals and the shifting were attributed to existing interactions between the IL and ethanol. Results of ^1H NMR indicate that the chemical structure of $[\text{HMim}][\text{HSO}_4]$ is preserved during the exposition to scEtOH. Analysis through MS showed that no significant change in chemical structure of IL occurred due to exposition to scEtOH. The MS spectra [positive mode: (a); negative mode: (b)] are presented in Fig. 3 and confirm the results achieved by ^1H NMR.

Positive mode of MS spectra shows peaks at m/z 83 and 111. The peak at m/z 83 represents the positive ion of the ionic liquid which, in this case, is the alkyl imidazolium ring. The peak at m/z 111 represents the positive part of the IL that was coupled to ethyl group from the ethanol molecule during to the exposition to scEtOH (9.62 MPa and 528 K). On the other hand, the peaks at m/z 125, 97, 89 and 62 were observed in the negative mode of the MS spectrum. The peak at m/z 125 represents the negatively-charged part of the IL that was coupled to the ethyl group from the ethanol molecule. The peak at m/z 97 represents the negatively-charged part of the IL by itself. These results indicate that $[\text{HMim}][\text{HSO}_4]$ was chemically stable as exposed for 45 min to T and P conditions of supercritical ethanol.

3.2. Products obtained from the transesterification of waste cooking soybean oil under scEtOH catalyzed by $[\text{HMim}][\text{HSO}_4]$

The expected products from transesterification reaction of soybean waste oil under scEtOH were ethyl esters and either glycerol, monoacylglycerols, diacylglycerols and triacylglycerols. If the reaction is complete, each triglyceride molecule must form three alkyl esters and a glycerol molecule. As ethanol is used, as in the case of this work, ethyl esters should be found as products.

The presence of all these products after transesterification reaction of soybean waste oil under scEtOH using IL $[\text{HMim}][\text{HSO}_4]$ as catalyst was evaluated. Data from GC and ^1H NMR proved that ethyl esters were formed in greater quantity, so as the main products.

In general, increase in temperature accelerates the reaction leading to higher yield. As the transesterification reaction is conducted at high temperatures, e.g. at scEtOH, as in this work, the molecules within the reactor vessel move speedily, allowing the increase of probability for collisions among reactants [50]. In this case, the reactants are oil and alcohol molecules.

3.3. Activity of $[\text{HMim}][\text{HSO}_4]$ during transesterification

There is a consensus that hydrolysis and alcoholysis of esters are too slow because the ester carbonyl and the nucleophilic agent are little reactive and the leaving group of the ester is a strong basis. Due to this, for increasing the reaction speed, these reactions are, often, catalyzed by acids or bases [51,52].

Ionic liquids (IL), as catalysts, provide alternative pathway by which IL-catalyzed reactions may occur speedily, for example, allowing the formation of carbocations, carbanions, and other electrically charged intermediates [53]. So, ILs enable formation of more stable complexes that have longer lifetimes in a given reaction media by decreasing the free energy of the reaction, enhancing the reaction rate [54].

In certain cases, ILs are more attractive than water and conventional organic solvents due to IL's properties like non volatility and also thermal and chemical stabilities. Moreover, they can be reused without significant loss in catalyst activity [55]. $[\text{HMim}][\text{HSO}_4]$

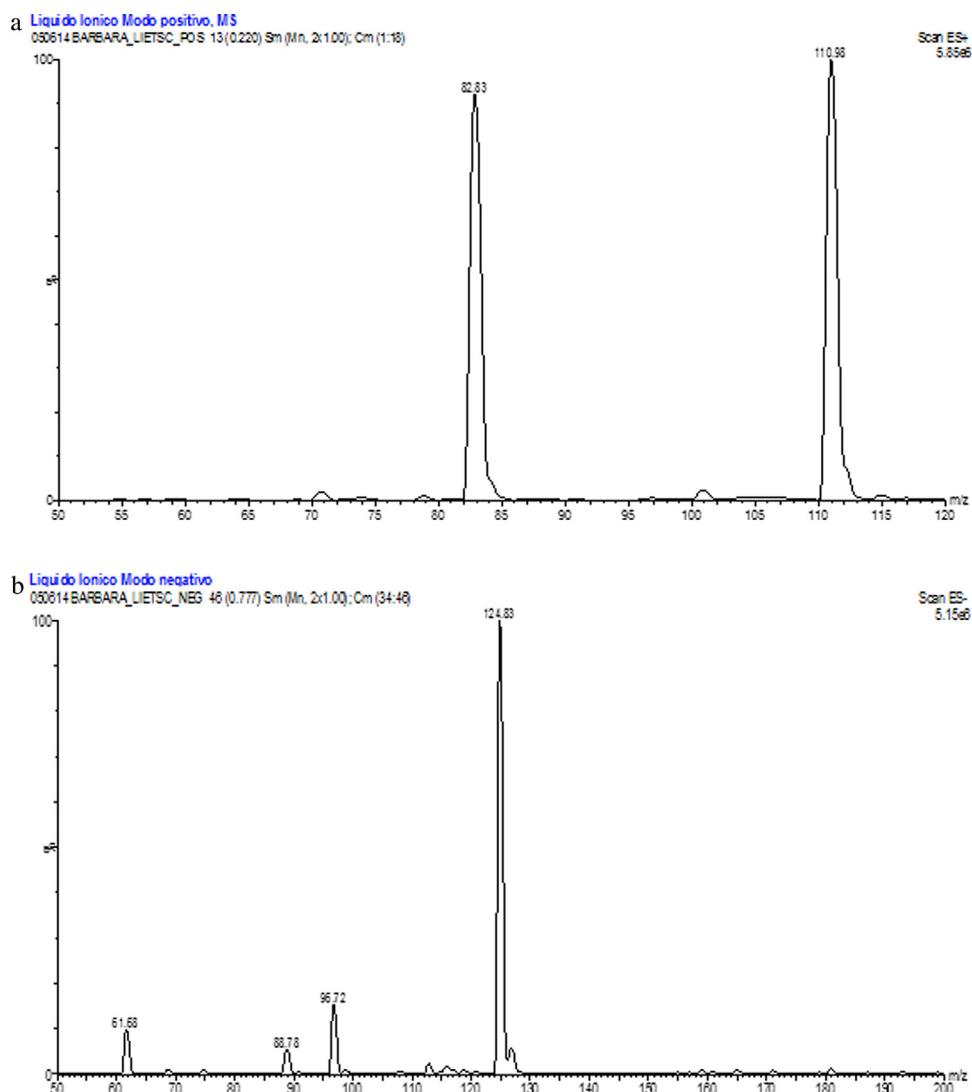


Fig. 3. Mass spectra of $[\text{HMim}][\text{HSO}_4]$ after 45 min of exposure in: (a) positive mode; and (b) negative mode.

showed significant activity during chemical depolymerisation by scEtOH [43].

To evaluate the $[\text{HMim}][\text{HSO}_4]$ catalyst capability, transesterification reactions of soybean waste oil without the use of catalyst were also performed in this work. The yield was near 85% on the 45 min reaction however, it is worthy to say that in the 0 min reaction, the transesterification doesn't occur without the catalyst presence. This assures that the high yields of ethyl esters formation, as described, are due to the catalyst capability of $[\text{HMim}][\text{HSO}_4]$ as submitted to scEtOH conditions (pressure and temperature) as used in this study. The acidic character of IL $[\text{HMim}][\text{HSO}_4]$ provided an increase in the yield of transesterification reaction in comparison to the reaction developed without catalyst.

The proposed mechanism for transesterification reaction products of waste cooking soybean oil, in acidic environment, as investigated in the present work, is shown in **Scheme 3** based in a paper published by Nunes et al. [43].

The quantity of catalyst was varied between 0.15 mL and 0.35 mL in the total of soybean waste oil added on the reactor. It can be noticed that the amount of IL employed did not exert significant effect on yielding of biodiesel produced.

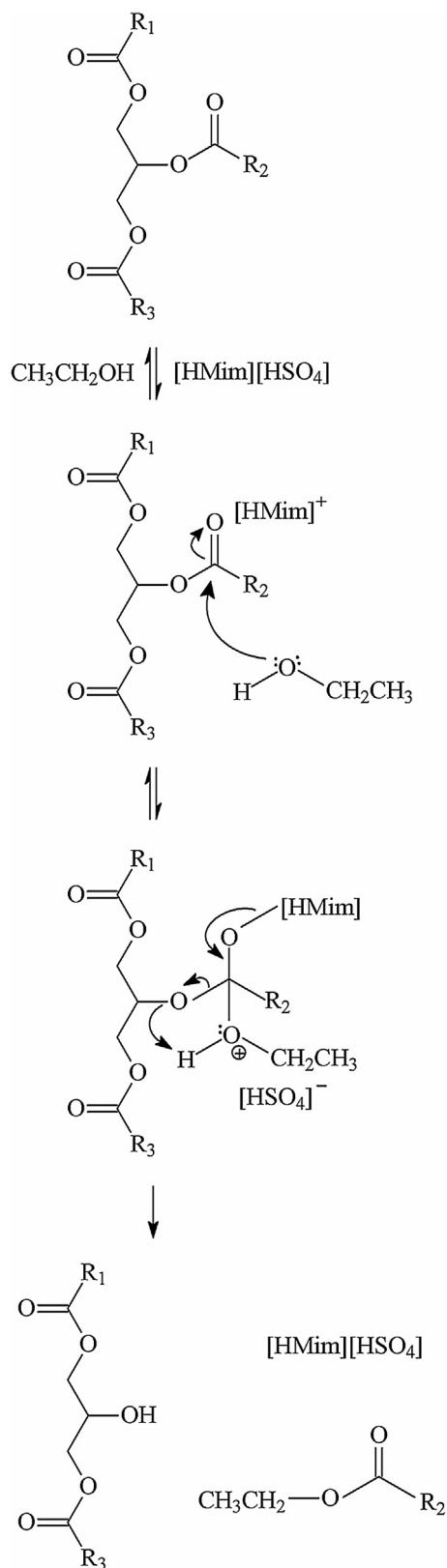
Furthermore, extra experiments performed in this study (under conditions not described in **Table 1**) showed that addition of water

to ethanol in the concentration range of 1.0–3.0% (v/v) did not influence the yield of biodiesel produced. There is great evidence that it is possible to use scarcely hydrated ethanol for producing ethyl esters through the methodology proposed in this work.

Some published works proposed procedures for biodiesel production using ILs, as catalysts, but without using supercritical conditions. For example, Xuezheng and Huiquan used waste oil and a solid acidic polymer ionic liquid (PIL) to generate biodiesel and the reaction yield was 99% after 12 h at 343 K [56]. Han et al. obtained yield of 93.5% after 4 h reaction at 443 K as acidic medium (Bronsted IL), methanol and waste oils were employed [57].

According to literature, supercritical fluids (specifically supercritical methanol and ethanol) have been used for transesterification reactions [15,58–61]. Using scEtOH but without IL on the transesterification, Gui et al. obtained yield of 79.2 mass% of biodiesel after reaction be performed for 30 min at 622 K [15]. Nan Y. et al. obtained yielding of 90.8 % and 87.8 % using methanol and ethanol during 31 and 35 min, at 593 K and 613 K; and 15.2 MPa and 17 MPa, respectively, on the biodiesel production from microalgae oil by non-catalytic transesterification [61].

Meloni et al. used guanidine base functionalized SBA-15 catalysis on the transesterification of soybean oil and obtained high fatty acid methyl esters yield (100 mol%) after 4 h of reaction [62]. Degir-



Scheme 3. Proposed mechanism for the transesterification under scEtOH in the presence of the IL [HMim][HSO₄], based on work of Nunes et al. [43].

menbasi et al. showed biofuel production via transesterification using sepiolite-supported alkaline catalysts, where methyl esters yield were about 98.5% with reaction time of 1–8 h [63].

Acid catalysts accelerate the transesterification/esterification reactions of free fatty acids and, furthermore, no soaps or emulsions is formed [62,64]. Soaps or emulsions occurs in basic medium and at high temperatures the saponification occurs prior the alcoholysis [65]. For example, on the biodiesel synthesis, Alegría et al. used triglycerides, methanol and 4-dodecylbenzenesulfonic acid to reach conversions next to 100 % in about 3 h [64] and Chen et al., used Ti-incorporated SBA-15 mesoporous silica as a solid catalyst for simultaneous esterification and transesterification of vegetable oils with methanol at 473 K for 3 h to achieve a content of 90 mass% in esters [66].

Therefore, the combination of scEtOH and acidic IL on transesterification reaction of soybean waste oil using mild conditions of *P* and *T*, as compared to methods already described, represents a good and sustained strategy for transesterification because achieved greater yields in lower reaction times. The combination of scEtOH and acid IL enabled shorter reaction times (less than 1 h) for near-complete transesterification of soybean waste oil with high yields. The reusability of catalyst, thus without chemical waste formation, comprises environmental and economic process requirements.

3.4. Characterization of main products through GC

The obtained chromatograms through GC showed characteristic peaks that after integration provided the relative amount (in percentage) of ethyl esters, mono-, di- and triacylglycerol in the samples collected after transesterification. The peak attributed to glycerol was not observed in the chromatograms indicating that it was completely removed in the washing step. It is expected due to high solubility of glycerol in water.

Chromatograms of products from transesterification reactions (runs 1–5) are presented in Fig. 4 in which the peaks attributed to ethyl esters appear in the elution time range from 8 to 13 min. Peaks with minor intensities appear in the elution time range from 13 to 15 min, 16 to 20 min and 20.5 to 23 min and they represent mono-, di- and triacylglycerol respectively [21,67].

Table 2 shows the percentage of ethyl esters obtained after transesterification reactions, calculated based on GC data. The values were calculated according to the methodology previously proposed by Visentainer and Franco [45].

All the experiments produced great amount of ethyl esters. Run 4 presented the smaller percentage of biodiesel obtained (93.58 %), but the decrease is less than 5% when compared with the run 1 (97.59 %), where the highest amount of ethyl ester was obtained. Recovered IL [HMim][HSO₄] was used as catalyst in run 5. It can be noticed that the catalyst capability is not decreased. Using the recovered IL the yielding is more than 95%.

3.5. Characterization of the main product through ¹H NMR spectroscopy

In the ¹H NMR spectrum of soybean waste oil not submitted to transesterification, showed on Fig 5, there are signals on range from δ 4.00 to 4.40 ppm attributed to H atoms of α -methylene groups of the triacylglycerol (TAG; two doublet of doublets **a** and **a'**) [20,21], while in the same region between 4.00 and 4.40 ppm of ethyl ester spectrum, signals associated with the α -methylene groups of the long chain ethyl esters (quartet **a''**) appeared [21,22]. ¹H NMR spectra of soybean waste oil and ethyl esters show signals almost at the same place (on the range of 4.00–4.40 ppm) and an overlap of these signals would occur in the case of the conversion of soybean to ethyl ester was not 100% effective. Such overlapping hinders the quantification of the main product (ethyl ester in this case) because

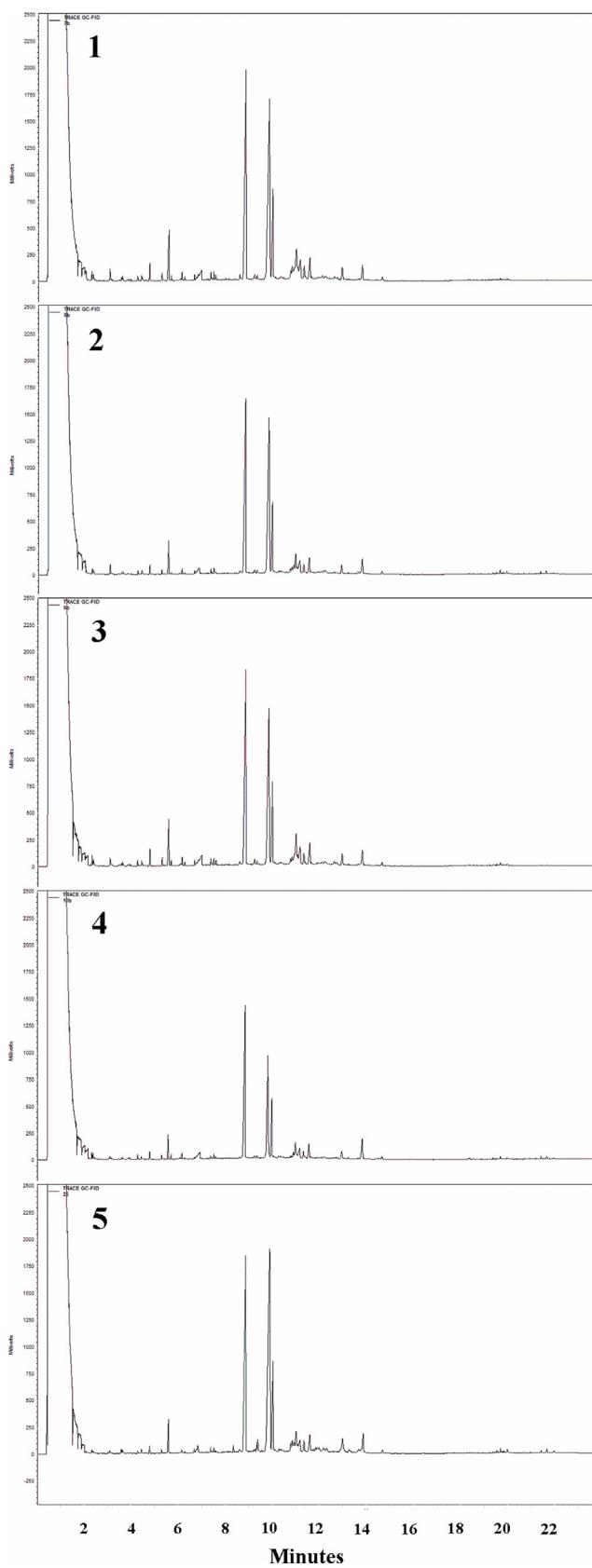


Fig. 4. GC chromatograms performed using products from runs 1–5 (Table 1).

Table 2
Percentage of ethyl esters formed during transesterification reaction in runs 1–5.

Run	% Ethyl esters
1	97.59
2	96.24
3	97.16
4	93.58
5 ^a	95.12

Experimental condition: pressure: 9.62 MPa; temperature: 528 K; volume of catalyst: 0.35 mL; volume of ethanol: 60 mL; oil weight: 1.5 g.

^a Recovered catalyst.

it becomes impossible to obtain the real integration value of the interested peak.

Analyses of ^1H NMR spectra (300 MHz, CDCl_3) showed in Fig. 5 allow noticing that it is possible to transform almost 100% of soybean waste oil to ethyl esters using the proposed methodology. Signals between 4.00 and 4.40 ppm attributed to the hydrogen atoms from the triacylglycerol α -methylene groups are not observed on ^1H NMR spectra of samples from runs 1 to 5. If one component is present in a given sample at too small relative concentration, the error associated to the such measure should be high [68]. So, as the peaks referred to triglycerides of soybean waste oil are too small and overlapped to the baseline, it can be inferred that the amount of triglycerides remained on the biodiesel sample can be neglected. In this way, based on ^1H NMR data and in the above discussion, it can be pointed out that ethyl esters were almost completely formed from the soybean waste oil with high yields ($\sim 100\%$).

3.6. Influence of reaction time on transesterification reaction under scEtOH

The influence of reaction time on yield of transesterification reaction of soybean waste oil under scEtOH catalyzed by $[\text{HMim}][\text{HSO}_4]$ was investigated performing the reaction in four different reaction times (Table 1). Using both ^1H NMR and CG analysis, it was possible to find that almost the same yield was achieved in all investigated reaction times: 45, 30, 15 and 0 min (run 1–4).

It is worthy to say that in the reaction set as time = 0 min is the moment that the chronometer for counting the reaction time was triggered and it is just after the moment that the system achieved the scEtOH condition (9.62 MPa and 528 K). It means that in run 4 (reaction time = 0 min) the system stayed above that condition, i.e., it had achieved subcritical and not the scEtOH conditions. In spite of this, ethyl esters were formed in considerable amount (yield = 93.58%). Thus, the subcritical condition seems to be auspicious.

The analysis of the data from Table 2 shows that supercritical conditions is more preferable for ethyl esters forming because there is a slight increase in ethyl ester yield after the system achieved the supercritical conditions (reaction time > 0 min). But in the reaction time range > 0 min the values of yield remain almost constant, close to 96%. So, it can be inferred that at scEtOH there is an equilibrium in the transesterification reaction.

It means that longer times are not necessary for increasing the yielding related to ethyl esters formation by the methodology presented in this work. Literature data show some transesterification reactions that spend too much time to occur. For example, Brusamarello et al. studying the kinetics of lipase-catalyzed synthesis of soybean fatty acid ethyl esters in pressurized propane and Lee et al. converting restaurant grease to esters by alkali-catalyzed methanolysis, developed during 8 and 24 h reaction times [69,70].

Some authors had presented transesterification reactions under supercritical fluids performed at severe conditions of temperature and pressure. For instance, Nan et al. studied the biodiesel

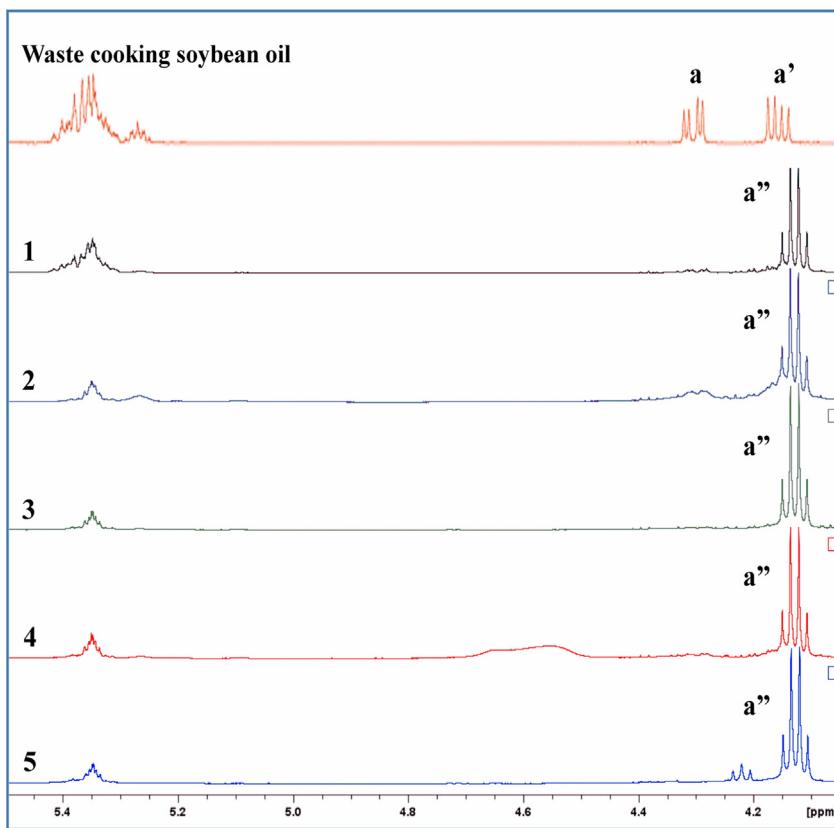


Fig. 5. ^1H NMR spectra, from waste cooking soybean oil and ethyl esters of long chain, formed after transesterification reaction. (300 MHz, CDCl_3).

production under methanol supercritical conditions and still tried many different alcohols (ethanol, 1-propanol, 1-butanol, 1-octanol) in the reaction, using reaction temperature set at 573 K to all the experiments [61]. Their results demonstrated that the alkyl esterification had higher reaction rates compared to the transesterification. He et al. used pressure and temperature of 35 MPa and 583 K, respectively, and gradual heating from 373 K up to 613 K for continuous transesterification of vegetable oil using supercritical methanol [59]. Ong et al. used leather tanning waste for biodiesel production through transesterification at supercritical condition performing the experiments in bath system at various temperatures, from 523 K to 598 K, under pressure of 12 MPa [59,60,71]. Vieitez et al. evaluated the stability of ethyl esters from soybean oil as exposed to supercritical ethanol at different temperatures, from 523 K to 648 K. Quesada-Medina et al. in the work dealing to degradation products from thermal decomposition of methyl esters fatty acid during the synthesis of biodiesel under supercritical methanol showed that thermal decomposition of the as-obtained fatty acids chains occurs just above 573 K [72,73].

In practice, despite transesterification reactions have been achieved in these studies, such processes are not easy to operate due to the severe reaction conditions. In comparison, our study uses relatively lower T and P conditions, allowing the ethanolysis being easier to perform. The process described in this work combines IL and supercritical ethanol for transesterification of waste of soybean oil, being a novelty and alternative for waste cooking oil reuse in a friendly-environmental process with perspective for technological applications.

4. Conclusions

The use of supercritical ethanol (scEtOH) combined to ionic liquids (IL) showed to be promising methodology for the ethyl esters

production from the soybean waste oil. The ethanol is renewable and the catalyst can be recovered and reused. Results showed that this reaction might be an interesting process and that it is technically potential to replace common catalysts.

The transesterification reaction produced ethyl esters as main products in all the studied reaction times. Quantification of these products was done by GC and ^1H NMR techniques being the yields higher than 95%. Catalysis promoted by the IL [HMim][HSO₄] was verified because it provided high yielding. Therefore, the proposed methodology using soybean waste oil as work material can be performed following the principles of green chemistry and show potential of industrial application. More studies are necessary to optimize the process to allowing warranties for production scale.

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